APPLICATION

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METHOD FOR RECOVERING AN ORGANIC SOLVENT FROM A WASTE STREAM CONTAINING SUPERCRITICAL CO_2

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FIELD OF THE INVENTION

The present invention relates to a method for recovering an organic solvent from a waste stream containing the organic solvent, supercritical carbon dioxide (CO_2) and other contaminants. The method of the present invention is especially useful for treating waste streams that contain supercritical CO_2 and the organic solvent along with contaminants from etching in fabricating integrated circuit products. The organic solvent of especial interest according to the present invention is propylene carbonate.

BACKGROUND OF INVENTION

In the fabrication of microelectronic components, a number of the steps involved, for instance, in preparing integrated circuit chips and the packaging for the chips (articles to which the chips are attached and protected) are etching processes. Accordingly, over the years, a number of vastly different types of etching processes to remove material, sometimes in selective areas, have been developed and are utilized in varying degrees. Moreover, the steps of etching different layers which constitute, for instance, the finished integrated circuit chip, are among the most critical and crucial steps.

One method widely employed for etching is to overlay the surface to be etched with a suitable mask and then immerse the surface and mask in a chemical solution which attacks the surface to be etched, while leaving the mask intact and while only etching other materials of the article to at most, a minimum extent.

Recently, selective etch processes employing etching compositions comprising supercritical CO_2 and an organic solvent, preferably propylene carbonate, have been

developed and suggested for etching various materials. Use of these compositions has provided improved properties such as a wider process window as well as enhanced selective performance.

However, use of these etching compositions results in waste streams containing the supercritical CO_2, organic solvent, and a wide variety of etchant contaminants such as silicon dioxide, silicon nitride, ammonium fluoride (NH_4F) and the like.

It would therefore be desirable to provide a method for treating the waste stream at least from both economic and environmental viewpoints. Moreover, proper recovery of the solvent would yield for reuse, a superior etchant as regards process control and function.

SUMMARY OF INVENTION

The present invention relates to a method for treating a waste stream that contains both supercritical CO_2 and an organic solvent to remove the supercritical CO_2 and recovery the organic solvent. In particular, the present invention provides a method that is reasonable from an economic viewpoint for recouping and repurifying the organic solvent in the contaminated waste stream. Accordingly, the present invention is beneficial from an ecological viewpoint along with reducing or avoiding waste disposal, reducing waste disposal costs, and reducing raw materials purchase costs.

In particular, the method of the present invention relates to treating a waste stream that comprises supercritical CO_2, an organic solvent and non-volatile etchant contaminants by separating the supercritical CO_2 from the waste stream to thereby obtain a first composition containing the supercritical CO_2 and a second stream containing the organic solvent and being free of the supercritical CO_2. The separation can be carried out subjecting the waste stream to elevated temperatures and/or reduced pressure.

Next the etching contaminants are removed from the second stream containing the organic solvent to recover the organic solvent free of the etching contaminants. Typical processes that can be used for this purpose are evaporation, distillation, filtration, centrifugation and settling.

Still other objects and advantages of the present invention will become readily apparent by those skilled in the art from the following description, wherein it is shown and described preferred embodiments of the invention, simply by way of illustration of the best mode contemplated of carrying out the invention. As will be realized the invention is capable of other and different embodiments, and its several details are capable of modifications in various obvious respects, without departing from the invention. Accordingly, the description is to be regarded as illustrative in nature and not as restrictive.

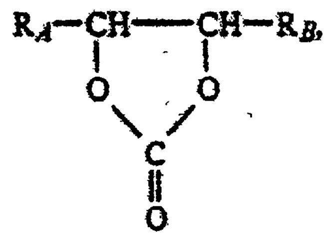
SUMMARY OF DRAWINGS

The figure is a flow diagram illustrating various alternative procedures for separating the supercritical CO_2 from the waste stream and organic solvent.

Best and Various Modes for Carrying Out Invention

The etching compositions which are used and subsequently result in the waste streams treated according to the present invention comprise supercritical CO_2 and an organic solvent. The organic solvent employed includes oxolanes, sulfoxolanes, esters, ketones, aldehydes, lactones, halogenated solvents, amines, imides and monohydric alcohols. Examples of suitable esters are esters of carboxylic acids, benzoic acid, phthalic acid, isophthalic acid and terephthalic acid, and especially the C_1-C_6 alkyl esters. Preferred organic solvents are propylene carbonate, homologs of propylene carbonate, N-methyl pyrrolidone, gamma butyrolactone, methylene chloride, benzyl alcohol, N-formyl morpholine, N-formyl piperidine, cyclohexanone, cyclopentanone, methyl benzoate, diglyme, 2-methyl tetrahydrofuran, and methyl and ethyl esters of phthalic, isophthalic or terephthalic acids. The more preferred solvents employed are propylene carbonate, N-methyl pyrrolidone and gamma butyrolactone, with propylene carbonate, and homologs thereof being the most preferred.

Examples of homologs of propylene carbonate can be represented by the formula:



where R_A and R_B are short chain alkyl groups or hydrogen. Exemplary short chain alkyl groups are $CH_3-(CH_2)_n-$, where n in R_A and R_B are independent integers from 0 to 3.

The compositions typically contain about 0.1 to about 3 molar of the supercritical CO_2 and the remainder being the organic solvent.

These etching compositions, depending upon various modifications such as are used to etch various materials such as silicon nitride, various silicon dioxides, and ammonium fluoride *inter alia*.

Accordingly, the waste stream from the etching process contains supercritical CO_2, and the organic solvent, preferably propylene carbonate, along with etchant contaminants such as silicon dioxide, silicon nitride, and/or ammonium fluoride. In addition, in the event water was present in the etchant composition, or otherwise became incorporated during etchant use, such will likewise be present in the waste stream.

Reference to the figure illustrates an embodiment of the present invention along with various alternatives suitable for carrying out the process of the present invention. In particular, the figure illustrates conveying the waste via conduit 12 to a preheater or evaporator 13. If desired as an optional step, deionized water can be added to the evaporator 13 via conduit 14 to help reduce the loss of solvent there. The evaporator 13 is run at temperatures, times and pressures sufficient to expel the CO_2 (such as under vacuum).

The temperature and pressure conditions required to remove the CO_2 depend on the identity of the particular solvent being used and the degree of removal which must be achieved. Typically, temperatures are about 20°C to about 150°C; pressures are about 15 torr to about 760 torr. When the solvent is propylene carbonate, temperatures are typically about 20°C to about 130°C and pressures are about 15 torr to about 75 torr. In the preferred embodiment, which uses propylene carbonate, the most preferred temperature is 120°C and, the most preferred pressure is about 25 torr. The residence time of the waste at these

conditions would vary with the removal requirements; which typically is about one second to about one hour. In the next preferred embodiment, residence time in the evaporator is about 10 seconds. The CO_2, and other volatiles, and water are removed via conduit 15 and the organic solvent along with any waste solids that might be carried with it is removed via conduit 16.

The stream via conduit 16 can be fed to an evaporator, especially a wiped film evaporator (WFE) 17 to separate remaining waste solids from the organic solvent. The waste solids are removed at exit 18 and the organic solvent is removed at conduit 19.

If desired, a plurality of evaporators 17 as shown in the figure can be employed to help improve solvent yield.

Solvent from the evaporators can be conveyed such as via conduit 19 to a condenser 20.

In the alternative or in addition thereto, the stream can be conveyed to a filtration means 30 or centrifuge process 31 or settling process 32 to separate waste solids from the organic solvent. Other means might also be applied. The particular parameters for these processes can be determined by persons skilled in the art and aware of this disclosure. For instance, for a filtration process, such design factors as sequential filtration, pore size, surface area, and materials of construction are considered by the user to optimize operating factors (such as flow rate, pressure drop, and service life) with desired product quality. For a centrifuge process, factors such as rotational speed and residence time are considered relative to etchant media characteristics. For a setting process, factors such as residence time, superficial velocity, and available space are considered.

The solvent from any of these processes can then be conveyed such as via conduit 33 to storage via conduit 21. In the alternative, the solvent can be conveyed via conduit 22 to a fractionation unit 23 to undergo fractional distillation. This results in an organic solvent fraction being removed via exit 24 and sent to storage and water and other low boiling volatiles and gases being removed at exit 25 and sent to condenser 26.

The foregoing description of the invention illustrates and describes the present invention. Additionally, the disclosure shows and describes only the preferred embodiments of the invention but, as mentioned above, it is to be understood that the invention is capable of use in various other combinations, modifications, and environments and is capable of changes or modifications within the scope of the inventive concept as expressed herein, commensurate with the above teachings and/or the skill or knowledge of the relevant art. The embodiments described hereinabove are further intended to explain best modes known of practicing the invention and to enable others skilled in the art to utilize the invention in such, or other, embodiments and with the various modifications required by the particular applications or uses of the invention. Accordingly, the description is not intended to limit the invention to the form disclosed herein. Also, it is intended that the appended claims be construed to include alternative embodiments.